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SIMULTANEOUS EPITAXY OF SILVER ONTO
TWO DIFFERENTLY ORIENTED L:F CRYSTALS

CHARLES J. MOORE

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Charles J. Moore

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by

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Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

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This work is accepted as fulfilling
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MASTER OF SCIENCE

IN

PHYSICS

from the

United States Naval Postgraduate School

ABSTRACT

Pairs of thin silver crystals, 20,000 to 60,000 Å⁰ thick, with different lattice orientations have been grown by epitaxial condensation in a single evaporation. Pair orientations were all combinations of the (100), (111), (110) and (112) planes parallel to film surface. Strong preferential orientation was obtained and pair mass thickness differences of 1-2% or less were achieved by using substrate temperatures in the general range 430°C to 470°C. The results indicate that condensation sticking coefficients for Ag on LiF are at most weak functions of temperature and orientation.

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1. INTRODUCTION

The ordered depositing of atoms onto a crystal substrate in an extension of the substrate lattice is the phenomenon known as epitaxy. Epitaxy may take place in a solution or as an evaporation-condensation process.

Epitaxial condensation from the vapor phase was first observed by H. Lassen about 1934 and the preparation of preferentially oriented crystal films of metals and other substances by this effect was first studied by his student, Von L. Bruck (1), in 1936. It has subsequently been studied by many workers and a comprehensive review of the topic was presented by Pashley (2) in 1956. Condensation of metals onto an ionic crystal substrate provides a convenient method of obtaining thin films having good lattice regularity. While the physics underlying such epitaxial growth is not completely understood, the "state of the art" is well advanced.

To induce epitaxial condensation, it is necessary to prepare the substrate carefully and preheat it to varying epitaxial temperatures prior to evaporation and condensation. This preheating serves to leave the condensing atom with sufficient mobility to move about on the substrate surface until it reaches a preferred location. Basset and Pashley (3) examined gold deposits of varying thicknesses 500\AA and less on sodium chloride crystals and found nucleation centers forming and growing as the evaporation continued until they joined to form a continuous surface. This process may result in stacking faults at the nucleation joints. In the case of the (III) orientation for face centered cubic crystals, twinning is also

possible.

Certain relations may be required between the lattice parameters of the substrate and the condensate, but what these are is not well established. One such relation is percentage misfit, defined as $100(b - a)/a$, where a and b are corresponding lattice spacings in the substrate and deposited material. Deposits of face centered cubic metals on ionic crystals have been successful with percentage misfits as high as 105% and have been unsuccessful under other circumstances with very small misfits. Furthermore, crystals have been grown having an orientation different from the substrate.

Several theories (2) have been developed to explain formation dependence on misfit and substrate temperature in relation to properties of the two materials involved, but the result is that there is no satisfactory general theory of epitaxy at this time and the process necessarily remains an art. However, it is well established that epitaxy temperatures are higher for substances with higher melting points.

This paper presents a technique developed to grow two silver films of different orientations simultaneously, achieving near-identical thickness of the two films. The prepared films are 20,000 to 60,000 Å thick and ultimately are to be used in measuring the range of protons in silver crystals and in basic sputtering experiments. The general apparatus and procedure are similar to those employed by Hall and Thompson (4) in 1960 for condensing silver onto lithium fluoride.

2. SUBSTRATE PREPARATION

Lithium fluoride crystals were used as a substrate for all orientations studied. The crystals obtained were 1 inch in diameter and 3-6 mm thick, with faces sawed parallel to (100), (110), (111) and (112) planes. Upon receipt, orientation of the faces was verified to be within 2° of the stated value by Laue diffraction patterns, analyzed by stereographic projection in the case of the (112) crystals and by comparison with standard Laue patterns for the more symmetric (100), (110) and (111) orientations.

The crystals were polished as smooth as possible using a 3 micron diamond wheel and afterwards cleaned in alcohol. Then they were etched in 48% hydrofluoric acid for approximately 60 seconds, and rinsed, first in water, then alcohol and finally ether, for fast drying. The etched crystals were chemically polished in a strongly stirred mixture of 4 ml of stock ammonium hydroxide solution (about 30%) and 196 ml of distilled water for periods of at least 5 minutes, depending on the freshness of the solution. It was usually necessary to replace the NH_4OH solution after polishing 4 crystals.

The crystals were again rinsed in alcohol and ether and stored in a sealed can with silica gel to await use.

3. APPARATUS

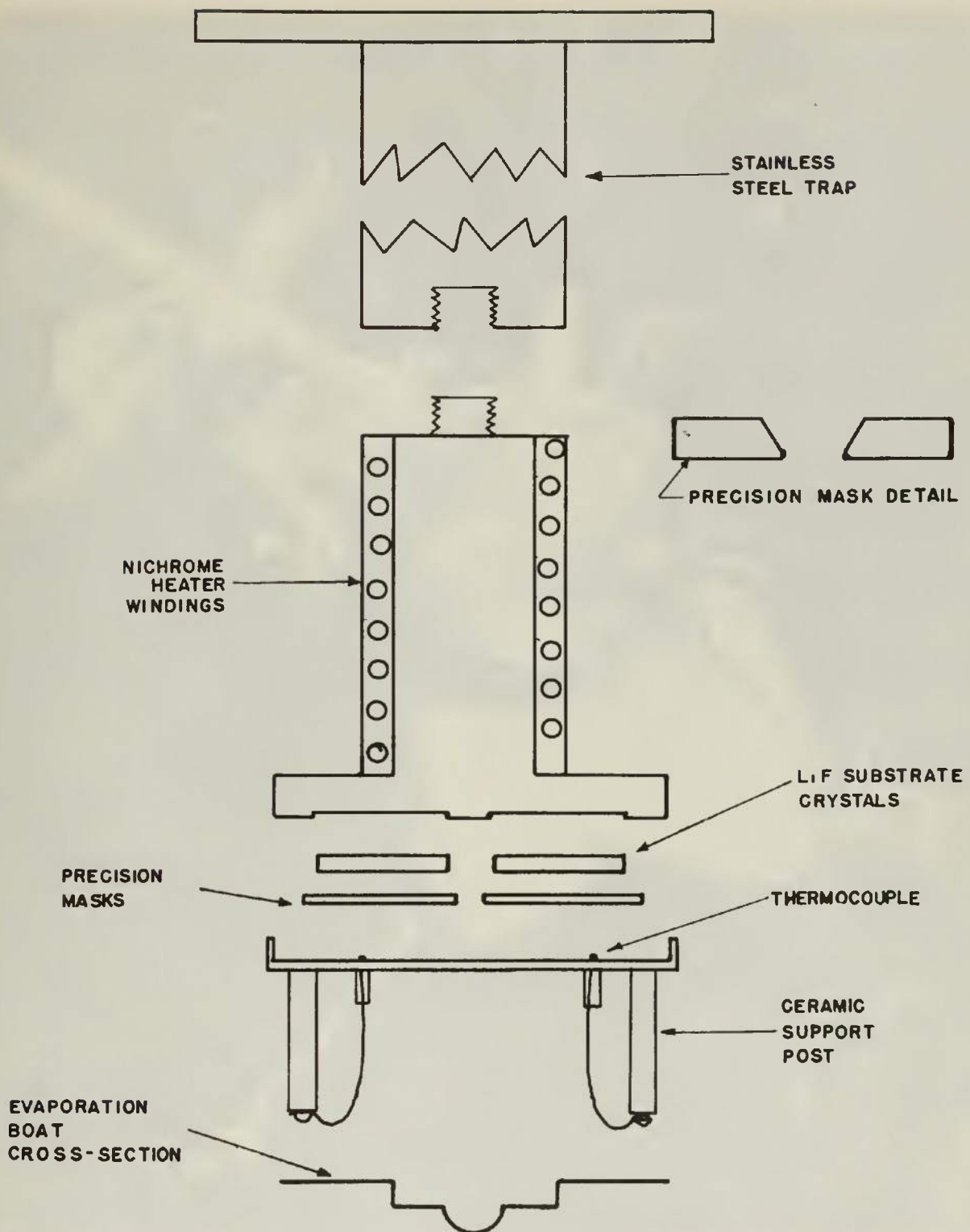
The LiF substrate crystals were clamped to a copper furnace for heating. Figure 1 shows a schematic drawing of the furnace assembly. Two precision shaped Cu masks were placed on the LiF and clamped to the furnace by a larger mask, each precision mask containing 3 holes which were hand reamed to 8 mm diameter. The sides of each hole were beveled as shown in plate 1 to prevent shadowing the growing area. About 0.5 mm of vertical wall was left.

Attaching the assembled furnace to the bottom of a stainless steel trap by threads provided both structural support and a metal-to-metal contact for rapid cooling. The mass of the furnace and trap was minimized to increase the cooling rate.

One thermocouple was placed against each LiF crystal through one of the holes and held gently in place during heating and cooling by a titanium spring. A flat bead was used to avoid penetrating the crystal.

Figure 2 shows a face view of the assembled furnace with one of the thermocouples in place. The four electrodes shown were used to measure the thickness of the silver film being deposited by effectively measuring the resistance of a narrow strip of silver about 1 1/2 inches along.

Figure 1 also shows a side view of the boat used. The four 90° corners were needed to allow the tantalum to expand when heated without moving the boat out of position. A large boat with about 5/16 inch radius of curvature was used to prevent the 3-4 grams of silver used from over-



FURNACE ASSEMBLY

PLATE I



Figure 2. Face view of assembled furnace.

flowing onto the arms, thus destroying the required symmetry.

Figure 3 shows the completely assembled furnace mounted in the evaporation chamber.





Figure 3. Complete evaporation assembly.

4. EXPERIMENTAL PROCEDURE

Care was taken in assembling the furnace to place one hole of each precision mask toward the center of the furnace, insuring symmetry of all condensation surfaces. The thermocouples were placed in the center of the hole nearest the supporting post to avoid shadowing the other two holes and to minimize any effects of temperature gradients across the substrate surface.

The center of the furnace was aligned over the center of the boat by sighting along two vertical lines at right angles. Boat to substrate separation was set at about 12 centimeters as a compromise between the need for a point source and the increased amount of silver required to be evaporated in order to obtain the desired thickness.

Silver used was spectrographically analyzed by the supplier and represented to be 99.999% pure. A shield was placed between the furnace and boat until the silver had melted and volatile impurities had evaporated. It had a soft iron counterweight which permitted it to be moved externally with a magnet.

Temperature of the substrate surfaces was raised to the epitaxial range and after it had stabilized, the silver was evaporated at the rate of about two grams in 15 minutes.

The boat and furnace heater currents were turned off after completion of evaporation, and the assembly was allowed to cool slowly to about 400°C. At this temperature water was poured into the stainless steel

trap and about 5 torr of Helium was admitted to the chamber, now sealed off from the pumps. This procedure resulted in initial cooling rates of about 25°C per minute and assisted the removal of the Ag film from the substrate by exploiting the difference in thermal expansion coefficients of the two materials and minimizing the time in which the silver could creep to accommodate the strain, rather than tear loose from the LiF lattice. Liquid air was substituted for the water as a cooling agent at about 150°C .

After the assembly had reached room temperature, the crystals were removed and soaked for several hours in lightly stirred distilled water, which dissolved enough LiF to loosen the film so that it could be lifted off with tweezers.

Films were then weighed by a precision electrobalance, which reads easily to .002 milligrams, and mounted for examination by Laue X-ray patterns and subsequent use.

5. RESULTS

Epitaxy temperatures reported by Hall and Thompson were used as a guide but were known to be high for this application since their thermocouple was placed in the furnace metal. The temperatures reported here should be easily reproducible as they were measured directly on the substrate surface. Temperatures at which epitaxial growth occurred without the presence of the polycrystalline Debye-Scherrer rings in the Laue patterns are as follows:

(100) 423°C to 463°C

(110) 437°C to 458°C

(111) 436°C to 495°C

(112) 430°C to 470°C

Investigation of the full range of epitaxial temperatures was outside the scope of this paper, but all lower bounds are considered fairly good. Higher bounds are likely in the case of the (110) and (100) orientations.

The surprising aspect of these temperatures is that the epitaxial ranges overlap for all orientations. Hall and Thompson had studied these four orientations in the case of gold on LiF and reported the midrange for (110) and (111) to be 70°C above that for (100) and the midrange for (112) to be 150°C above that for (100), with range widths of about 50°C.

While the possibility of a usable range for (100) at a much lower temperature exists, epitaxy was quite limited at 379°C and poor at 412°C (see figure 8), yet excellent at 463°C (see figure 6).

In view of the overlap in epitaxy temperatures reported above, it was possible to grow all pairwise combinations of these four orientations simultaneously. The temperatures of the two substrates always differed. This is attributed to small differences in thickness (of the order of .01 in) which resulted in one crystal being clamped tighter than the other. This aspect might be used to control the relative temperatures of the two substrate crystals.

Calculations show that a misalignment of the boat and furnace centers by 2 mm would result in a mass difference of 1%, while if the boat were exactly positioned under the centermost hole of one mask, the mass difference should be about 5%, all other factors being equal.

Several test evaporations were made with two LiF crystals having the same orientation in order to determine if the arrangement of the apparatus was sufficiently symmetrical. It was possible to obtain mass differences of 1-2% or less consistently.

The following film pairs were obtained:

| Orientation | Temperature | Mass | Mass difference | Laue X-Rays Figure |
|-------------|--------------------|----------|-----------------|-----------------------|
| (111) | 443 ^o C | 1.559 mg | | |
| (112) | 430 | 1.537 | 1.4% | 4 |
| (110) | 458 | 1.992 | | |
| (112) | 446 | 1.929 | .36% | 5 |
| (100) | 463 | 1.757 | | |
| (110) | 437 | 1.757 | --- | 6 |
| (111) | 459 | 2.338 | | |
| (110) | 445 | 2.294 | 1.9% | 7 |
| (112) | 433 | 1.239 | | |
| (100) | 412 | 1.251 | 1.0% | 8 |
| (111) | 436 | 1.448 | | |
| (100) | 448 | 1.350 | 7.0% | 9 |

All pairs reported were symmetrically located on the two substrates. It should be possible to decrease mass differences by increasing the boat to substrate distance.

Some Laue patterns show the spots spread into radial lines. This is due to stress and plastic deformation introduced in removal from the substrate. It is possible that such a stressed lattice might be improved by annealing.

The fact that these small mass differences could be obtained gives rise to two very interesting observations: 1) there is little, if any, temperature dependence of the condensation sticking coefficient at epitaxial ranges, and 2) there is no perceptible dependence of the sticking coefficient upon lattice orientation of the substrate. Insufficient work is presented here to establish these two points, but certainly they are fairly raised by the results.



Figure 4. Laue transmission patterns of silver films having (111) orientation (upper) grown at 443°C with mass 1.559 mg and (112) orientation (lower) grown at 430°C with mass 1.537 mg.



Figure 5. Laue transmission patterns of silver films having (112) orientation (upper) grown at 446°C with mass 1.929 mg and (110) orientation (lower) grown at 458°C with mass 1.922 mg.



Figure 6. Laue transmission patterns of silver films having (100) orientation (upper) grown at 463°C with mass 1.757 mg and (110) orientation (lower) grown at 437°C with mass 1.757 mg.



Figure 7. Laue transmission patterns of silver films having (111) orientation (upper) grown at 459°C with mass 2.338 mg and (110) orientation (lower) grown at 445°C with mass 2.294 mg.

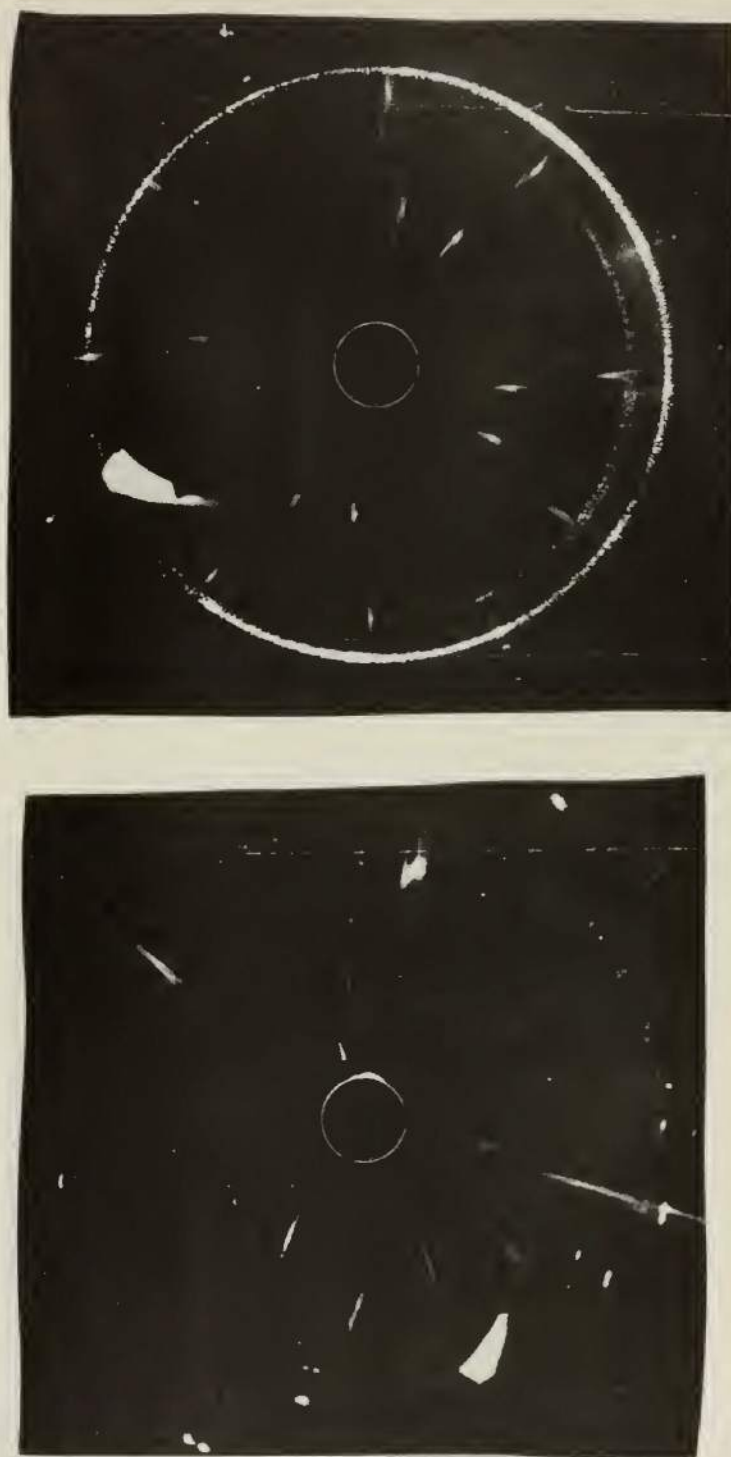


Figure 8. Laue transmission patterns of silver films having (100) orientation (upper) grown at 412°C with mass 1.239 mg and (112) orientation (lower) grown at 433°C with mass 1.251 mg.



Figure 9. Laue transmission patterns of silver films having (100) orientation (upper) grown at 448°C with mass 1.350 mg and (111) orientation (lower) grown at 436°C with mass 1.448 mg.

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